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(54) SEPARATOR FOR SEALED LEAD-ACID BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To further thin a profile and to efficiently apply to a flat plate electrode as well by enhancing density in a sealed lead-acid battery having enhanced strength against electrical short-circuiting between positive and negative electrode plates of a battery by mixing mainly a fine glass fiber with an inorganic powder and natural pulp.

SOLUTION: This separator is constructed of mainly a fine glass fiber and includes an inorganic powder and natural pulp beaten and decomposed. The content of the inorganic powder is 5-30 wt.%, the content of the natural pulp is 3-20 wt.% and the density is 0.165 g/cm3 or more. The fine glass fiber is an acid resistant glass fiber having an average diameter of 1 μ m or under.

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CLAIMS

[Claim(s)]

[Claim 1] The separator for sealed lead acid batteries characterized by for the content of this natural pulp being [for the content of these inorganic fine particles] 3 - 20 % of the weight at 5 - 30 % of the weight, and consistencies being three or more 0.165 g/cm in the separator for sealed lead acid batteries containing the natural pulp which was constituted as a subject and carried out beating of the detailed glass fiber to inorganic fine particles.

[Claim 2] The separator for sealed lead acid batteries characterized by this detailed glass fiber being an acid-proof glass fiber of 1 micrometer or less of diameters of average fiber in claim 1.

[Claim 3] The separator for sealed lead acid batteries characterized by these inorganic fine particles being the silica powder more than specific-surface-area of 100m 2/g in claim 1 or 2.

[Claim 4] The separator for sealed lead acid batteries with which this natural pulp is characterized by carrying out beating to 250 or less mL of Canadian freshness in claim 1 thru/or any 1 term of 3.

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DETAILED DESCRIPTION

[Detailed Description of the Invention] [0001]

[Field of the Invention] This invention relates to the separator for sealed lead acid batteries, and relates to the separator for sealed lead acid batteries which raised the resistance over the electric short circuit between the positive-electrode plate of a cell, and a negative-electrode plate especially by making a detailed glass fiber into a subject and mixing inorganic fine particles and natural pulp.

[0002]

[Description of the Prior Art] As a gestalt of the separator for sealed lead acid batteries, the sheet-like separator which mainly consists of glass fibers is common. However, with the conventional separator, the phenomenon of a positive-electrode plate and a negative-electrode plate short-circuiting electrically, consequently the charge and discharge of a battery becoming impossible with the crystal growth of the metal lead in the interior of the separator at the time of penetration by local pressure of a projection of a plate, or plasmotomy or charge etc., was seen. Since the conventional separator has the comparatively low mechanical strength, penetration, it being easy to carry out plasmotomy, and a consistency are comparatively low at the projection of an electrode, and since the aperture is comparatively large, it is because growth of the metal lead from a plate also tends to occur as for this, and if the thickness of a separator becomes thin, since a mechanical strength will fall upwards more and the distance between a positive electrode and a negative electrode will become short, such a phenomenon will become much more remarkable.

[0003] It is thought that the crystal growth of metal lead can improve among the causes of this electric short circuit by carrying out densification of the separator, decreasing an opening, and checking the crystal growth within a separator. As a means for that, it is possible to hold inorganic fine particles, such as a silica, for example between glass fibers. However, if inorganic fine particles are mixed, when a tangle of glass fibers decreases because the amount of part glass fibers becomes less, consequently a mechanical strength falls remarkably, the electric short circuit resulting from pressure of a projection of an electrode will become easy to occur.

[0004] On the other hand, penetration of a separator and plasmotomy improve by raising the mechanical strength of a separator. As a means for that, the approach of mixing a synthetic fiber is well-known (for example, JP,54-22531,A, JP,56-99968,A, JP,58-663,B). However, the separator which, as for the synthetic fiber, mixed the synthetic fiber since the hydrophilic property was low compared with a glass fiber has the fault that the absorbency of sulfuric-acid liquid and solution retention are inferior.

[0005] Moreover, a mechanical strength can be raised, without the approach of mixing a beating cellulose being also well-known (JP,64-52375,A), and spoiling absorbency and solution retention in this case. However, it cannot be only short circuit by the crystal growth of metal lead.

[Problem(s) to be Solved by the Invention] This invention is the separator for sealed lead acid batteries which raised the resistance over the electric short circuit between the positive-electrode plate of a cell, and a negative-electrode plate by solving the above-mentioned conventional trouble, making a detailed glass fiber into a subject, and mixing inorganic fine particles and natural pulp. The purpose is offering the separator for sealed lead acid batteries whose application made much more thinning possible and was enabled effective also in a plate electrode by raising a consistency.

[Means for Solving the Problem] In the separator for sealed lead acid batteries containing the natural pulp which was constituted as a subject and carried out beating of the detailed glass fiber to inorganic fine particles, the content of these inorganic fine particles is 5 - 30 % of the weight, the content of this natural pulp is 3 - 20 % of the weight, and the

separator for sealed lead acid batteries of this invention is characterized by consistencies being three or more 0.165 g/cm.

[0008] In many cases, the electric short circuit between the positive electrodes and negative electrodes in a sealed lead

acid battery occurs according to the following two causes.

[0009] [1] Mechanical short circuit: when projections (the irregularity of a grid, granular lump of an active material, etc.) are in a plate, the local pressure force and shearing force arise. As compared with this force, if the reinforcement of a separator is weak, penetration or plasmotomy occurs, and a projection will contact the plate of another side and will result in a short circuit.

[2] Electrochemical short circuit: if the sulfate ion in the discharge last stage and the electrolytic solution is consumed and the electrolytic solution becomes close to pure water, the solubility of lead ion will become large and a part of lead sulfate generated to the positive electrode and the negative electrode will dissolve. If it charges next, the lead ion in the electrolytic solution is returned with a negative electrode, and metal lead deposits. This crystal grows the inside of a separator, reaches the plate of another side, and results in a short circuit.

[0010] The short circuit by the cause of the above [2] is suppressed by making the path of the micropore of a separator small and carrying out densification by mixing inorganic fine particles, such as a silica, with the separator for sealed lead acid batteries of this invention. Furthermore, by mixing the natural pulp which carried out beating, the tensile strength and penetration-proof reinforcement of a separator are raised, and the short circuit by the cause of the above [1] is suppressed. Both, since these inorganic powder and natural pulp are the high ingredients of a hydrophilic property, they do not spoil the cell engine performance of a separator.

[0011] in this invention, it is based on two causes in this way -- simplistic -- since the separator which receives and has sufficient resistance can be milled at one process, it can manufacture by low cost.

[0012] And since the separator of this invention is comparatively high-density, thinning is possible for it, and an electrode spacing can apply it effective also in 0.3-0.7mm and a narrow plate electrode.

[0013] In this invention, as a detailed glass fiber, the acid-proof glass fiber of 1 micrometer or less of diameters of average fiber is desirable, and the silica powder more than specific-surface-area of 100m 2/g is suitable as inorganic fine particles. As natural pulp, that by which beating was carried out to 250 or less mL of Canadian freshness is desirable.

[0014]

[Embodiment of the Invention] The gestalt of the operation of this invention to the following is explained to a detail. [0015] The separator for sealed lead acid batteries of this invention makes a detailed glass fiber a subject, and a consistency is a three or more 0.165 g/cm thing including 5 - 30% of the weight of inorganic fine particles, and 3 - 20% of the weight of the natural pulp which carried out beating.

[0016] In this invention, as a detailed glass fiber, the acid-proof glass fiber of 1 micrometer or less of diameters of average fiber and alkali glass fiber with especially good acid resistance are desirable, and, as for the content of this detailed glass fiber, it is desirable that it is 50 - 92 % of the weight. If the diameter of average fiber of a detailed glass fiber exceeds 1 micrometer, liquid holding power, paper-milling nature, etc. will fall. Moreover, if less than 50 % of the weight of liquid holding power is [the content] insufficient and it exceeds 92 % of the weight, the content of inorganic fine particles and natural pulp will decrease relatively, and sufficient short circuit-proof nature will not be obtained. [0017] When less than 5 % of the weight of the content of inorganic fine particles is not enough as the short circuit prevention effectiveness and it exceeds 30 % of the weight, the rate of a detailed glass fiber or natural pulp decreases relatively, and a mechanical strength is inferior. Therefore, the content of inorganic fine particles is made into 5 - 30 %

[0018] As these inorganic fine particles, although a silica, a titanium dioxide, diatomaceous earth, etc. can be used, it is desirable to use the silica powder more than specific-surface-area of 100m 2/g by the high hydrophilic property from the point which is low cost. If it is the silica powder more than specific-surface-area of 100m 2/g, there is much pore on the interior of a particle and the front face of a particle, and it is excellent in the solution retention improvement

effectiveness of the electrolytic solution.

[0019] The content of the natural pulp which carried out beating cannot compensate enough the fall on the strength by inorganic powder mixing with less than 3 % of the weight, but the effectiveness over a short circuit is low. However, if this content exceeds 20 % of the weight, a separator will become hard too much and adhesion with a plate will fall. Therefore, the content of natural pulp is made into 3 - 20 % of the weight.

[0020] It is desirable to use what carried out beating of the pulp of a needle-leaf tree system with the beater etc. as this natural pulp. That is, needle-leaf tree system pulp can acquire the extremely excellent reinforcement effectiveness from fiber length being long and being homogeneous. When extent of the beating is expressed with Canadian freshness

(Canada standard freshness), it is desirable that 250 or less mLs are especially 150 or less mLs by 0.3-% of the weight concentration (in addition, the freshness of the natural pulp which has not carried out beating is 600 or more mLs.). If it is the natural pulp by which beating was carried out to such freshness, it has one several times the very big pore volume [usual specific surface area and pore volume] of pulp, and excels in reactivity, a hydrophilic property, water retention, etc., and acid resistance is also high, since it has the reinforcement effectiveness which was moreover excellent, the reinforcement and the degree of hardness of a separator can be remarkably increased by little addition, and solution retention and absorbency will not be spoiled.

[0021] In this invention, this natural pulp may substitute a fibrillation cellulose for that part. A fibrillation cellulose makes natural pulp detailed even to microfibril, and is effective in improvement in a mechanical strength. However, when blending a fibrillation cellulose, it is made for the loadings of the sum total with the natural pulp which made that content 5 or less % of the weight, and carried out beating to the fibrillation cellulose to become 20 or less % of the weight, since a separator will become hard too much and adhesion with a plate will fall, if the content of this fibrillation

cellulose exceeds 5 % of the weight.

[0022] The separator for sealed lead acid batteries of this invention can manufacture the above-mentioned component by following a conventional method, and mixing and milling paper preferably, or more [0.165g //cm] 3 consistency, so that it may become three or more 0.165 - 0.250 g/cm.

[0023] In this invention, the opening of a separator increases that the consistencies of a separator are less than three 0.165 g/cm, and when it considers as the separator for plate electrodes with thin thickness, sufficient short circuit-proof nature cannot be obtained. If a consistency becomes higher than 0.250 g/cm3, since solution retention etc. will fall, the consistency of a separator is preferably made into 0.165 - 0.250 g/cm3.

[0024] In this invention, even if it is the comparatively thin separator which it says is 0.4-0.8mm (thickness by the measuring method in the below-mentioned example) in thickness by considering as such a separator with a comparatively high consistency, sufficient short circuit prevention effectiveness can be acquired.

[0025] Such a separator for sealed lead acid batteries of this invention is very useful as a separator for plate electrodes.

[Example] Although an example and the example of a comparison are given to below and this invention is more concretely explained to it, this invention is not limited to the following examples, unless the summary is exceeded. In addition, the ingredient used in the following examples and examples of a comparison is as follows. [0027]

[Material of construction]

Glass fiber: 0.8 micrometers [of average fiber ****] alkali glass fiber Silica powder: Silica powder of specificsurface-area of about 200m 2/g Natural pulp which carried out beating: Needle-leaf tree system pulp Canadian freshness abbreviation 150mL What carried out beating Thermoplastic organic fiber: It is about 5m in 20 micrometers of average fiber ****, and fiber length. Polyester fiber The separator for batteries was manufactured by the ingredient combination shown in one to examples 1 and 2 and example of comparison 4 table 1, and measurement results, such as many of the properties, were shown in Table 1. In addition, each measuring method etc. is as follows. [0028] ** Thickness (mm) and a consistency (g/cm3)

It asked for thickness T (SBA4501) which measured the sample in the condition of having pressed by the pressure of 0.2 kgf/cm2 in the thickness direction, and the consistency was computed by W/(TxS) from the mass W measured with

this thickness T and an electronic balance, and the area S of a sample.

** Tensile strength (gf/10mm2)

It is based on SBA4501.

** Measure the maximum load at the time of forcing perpendicularly the needle which has a spherical tip at the rate of 120 mm/min to the fixed sample, and penetrating by 1mm of penetration sizes on the strength. Since this measured value was influenced by the form letter rack with a minute needle tip, relative evaluation was made on the result of the example 1 of a comparison as 100 in the ratio with the measured value in a standard sample (thing of the example 1 of a comparison).

[0029] ** Absorbency (mm/min)

A sample is made perpendicular, the lower part is immersed in the dilute sulfuric acid of specific gravity 1.30, and it asks by measuring the liquid level which goes up in 1 minute from the time of immersion.

[0030] ** Between the monotonous lead electrode plates (an electrode area of about 7mm 2) of two electrochemical short circuit duration, it arranges on both sides of a separator with a thickness of 0.5mm, and is immersed into the saturated solution of a lead sulfate. Furthermore, where the pressure force of 0.3 kgf/m2 is applied, regularity electricalpotential-difference 10V are impressed to this. If the metal lead which grew from the negative electrode reaches a

positive electrode, since inter-electrode resistance will decrease rapidly, this time amount is measured and it is the thickness of a separator, and it is ****. This measured value made relative evaluation on the result of the example 1 of a comparison as 100 in the ratio with the measured value in a standard sample (thing of the example 1 of a comparison).

[0031] Penetration reinforcement is the index of a mechanical short circuit among the above-mentioned characterization, and a mechanical short circuit cannot occur easily, so that penetration reinforcement is high. Moreover, electrochemical short circuit duration is excellent in the short circuit prevention effectiveness, so that it is long.

[0032]-[Table 1]

		実施例		比較例				
_		1	2	1	2	3	4	
配合(並量	ガラス繊維	80	75	100	80	75	90	
	シリカ粉末	10	20			20		
量 %	叩解パルブ	10	5				10	
	熱可塑性 有機緩維				20	5		
	厚さ (mm)	0.5	0.5	0.5	0.5	0.5	0.5	
特性等	密度 (g/am³)	0.18	0.20	0.14	0.15	0.20	0.15	
	引張強度 (gf/10mm²)	480	360	440	660	300	720	
	貫通強度 ※	190	120	100	270	70	200	

※ : 比較例1の結果を100とする相対値。

50

4500

吸液性

(mm/min)

電気化学的

短絡時間 ※

[0033] The following thing is clearer than Table 1.

50

6000

50

100

40

250

45

1600

[0034] That is, in the example 1 of a comparison of only a glass fiber, penetration reinforcement is low and its short circuit duration is also short. In the example 2 of a comparison of only a glass fiber and organic fiber, although penetration reinforcement is high, short circuit duration is comparatively short, and absorbency is also inferior in it. In the example 3 of a comparison which blended organic fiber with a glass fiber and silica powder, although short circuit duration is long, penetration reinforcement is very low. In the example 4 of a comparison of only a glass fiber and beating pulp, penetration reinforcement is high, and although absorbency is also good, short circuit duration is comparatively short.

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300

[0035] on the other hand, in the examples 1 and 2 which blended a glass fiber, silica powder, and beating pulp at a predetermined rate, without spoiling absorbency, high penetration reinforcement and long short circuit duration are filled to coincidence, and it is based on the two above-mentioned causes -- simplistic -- it receives and is very effective.

[0036]

[Effect of the Invention] According to the separator for sealed lead acid batteries of this invention, the following effectiveness is done so, the electric short circuit of the positive-electrode plate of a sealed lead acid battery and a negative-electrode plate cannot occur easily, it excels also in separator properties, such as absorbent ability, upwards, and the cheap separator for sealed lead acid batteries is offered as explained in full detail above. Especially the separator for sealed lead acid batteries of this invention is very effective in the thinning as a separator for high property plate electrode plates.

[0037] (1) Inorganic powder is held between the glass fibers of a separator, and it is high-density. The inorganic powder in the pore of a separator serves to bar the crystal growth of metal lead. Moreover, the microfilament of the natural pulp which carried out beating also carries out the same work. For this reason, the electric short circuit by the crystal growth of metal lead cannot occur easily.

(2) The natural pulp which carried out beating raises the mechanical strength, especially penetration reinforcement of a

separator. For this reason, penetration by the local pressure force in the projection of an electrode plate and plasmotomy cannot occur easily.

(3) Since it consists of only high ingredients of a hydrophilic property, a hydrophilic property and solution retention are high and the cell engine performance is good.

(4) It can manufacture easily at single mixing and a paper-milling process, and is low cost.

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TECHNICAL FIELD

[Field of the Invention] This invention relates to the separator for sealed lead acid batteries, and relates to the separator for sealed lead acid batteries which raised the resistance over the electric short circuit between the positive-electrode plate of a cell, and a negative-electrode plate especially by making a detailed glass fiber into a subject and mixing inorganic fine particles and natural pulp.

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PRIOR ART

[Description of the Prior Art] As a gestalt of the separator for sealed lead acid batteries, the sheet-like separator which mainly consists of glass fibers is common. However, with the conventional separator, the phenomenon of a positive-electrode plate and a negative-electrode plate short-circuiting electrically, consequently the charge and discharge of a battery becoming impossible with the crystal growth of the metal lead in the interior of the separator at the time of penetration by local pressure of a projection of a plate, or plasmotomy or charge etc., was seen. Since the conventional separator has the comparatively low mechanical strength, penetration, it being easy to carry out plasmotomy, and a consistency are comparatively low at the projection of an electrode, and since the aperture is comparatively large, it is because growth of the metal lead from a plate also tends to occur as for this, and if the thickness of a separator becomes thin, since a mechanical strength will fall upwards more and the distance between a positive electrode and a negative electrode will become short, such a phenomenon will become much more remarkable.

[0003] It is thought that the crystal growth of metal lead can improve among the causes of this electric short circuit by carrying out densification of the separator, decreasing an opening, and checking the crystal growth within a separator. As a means for that, it is possible to hold inorganic fine particles, such as a silica, for example between glass fibers. However, if inorganic fine particles are mixed, when a tangle of glass fibers decreases because the amount of part glass fibers becomes less, consequently a mechanical strength falls remarkably, the electric short circuit resulting from pressure of a projection of an electrode will become easy to occur.

[0004] On the other hand, penetration of a separator and plasmotomy improve by raising the mechanical strength of a separator. As a means for that, the approach of mixing a synthetic fiber is well-known (for example, JP,54-22531,A, JP,56-99968,A, JP,58-663,B). However, the separator which, as for the synthetic fiber, mixed the synthetic fiber since the hydrophilic property was low compared with a glass fiber has the fault that the absorbency of sulfuric-acid liquid and solution retention are inferior.

[0005] Moreover, a mechanical strength can be raised, without the approach of mixing a beating cellulose being also well-known (JP,64-52375,A), and spoiling absorbency and solution retention in this case. However, it cannot be only come out of the consistency change by mixing of a beating cellulose, and, for a certain reason, it cannot suppress the short circuit by the crystal growth of metal lead.

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EFFECT OF THE INVENTION

[Effect of the Invention] According to the separator for sealed lead acid batteries of this invention, the following effectiveness is done so, the electric short circuit of the positive-electrode plate of a sealed lead acid battery and a negative-electrode plate cannot occur easily, it excels also in separator properties, such as absorbent ability, upwards, and the cheap separator for sealed lead acid batteries is offered as explained in full detail above. Especially the separator for sealed lead acid batteries of this invention is very effective in the thinning as a separator for high property plate electrode plates.

[0037] (1) Inorganic powder is held between the glass fibers of a separator, and it is high-density. The inorganic powder in the pore of a separator serves to bar the crystal growth of metal lead. Moreover, the microfilament of the natural pulp which carried out beating also carries out the same work. For this reason, the electric short circuit by the crystal growth of metal lead cannot occur easily.

(2) The natural pulp which carried out beating raises the mechanical strength, especially penetration reinforcement of a separator. For this reason, penetration by the local pressure force in the projection of an electrode plate and plasmotomy cannot occur easily.

(3) Since it consists of only high ingredients of a hydrophilic property, a hydrophilic property and solution retention are high and the cell engine performance is good.

(4) It can manufacture easily at single mixing and a paper-milling process, and is low cost.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] This invention is the separator for sealed lead acid batteries which raised the resistance over the electric short circuit between the positive-electrode plate of a cell, and a negative-electrode plate by solving the above-mentioned conventional trouble, making a detailed glass fiber into a subject, and mixing inorganic fine particles and natural pulp. The purpose is offering the separator for sealed lead acid batteries whose application made much more thinning possible and was enabled effective also in a plate electrode by raising a consistency.

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MEANS

[Means for Solving the Problem] In the separator for sealed lead acid batteries containing the natural pulp which was constituted as a subject and carried out beating of the detailed glass fiber to inorganic fine particles, the content of these inorganic fine particles is 5 - 30 % of the weight, the content of this natural pulp is 3 - 20 % of the weight, and the separator for sealed lead acid batteries of this invention is characterized by consistencies being three or more 0.165 g/cm.

[0008] In many cases, the electric short circuit between the positive electrodes and negative electrodes in a sealed lead acid battery occurs according to the following two causes.

[0009] [1] Mechanical short circuit: when projections (the irregularity of a grid, granular lump of an active material, etc.) are in a plate, the local pressure force and shearing force arise. As compared with this force, if the reinforcement of a separator is weak, penetration or plasmotomy occurs, and a projection will contact the plate of another side and will result in a short circuit.

[2] Electrochemical short circuit: if the sulfate ion in the discharge last stage and the electrolytic solution is consumed and the electrolytic solution becomes close to pure water, the solubility of lead ion will become large and a part of lead sulfate generated to the positive electrode and the negative electrode will dissolve. If it charges next, the lead ion in the electrolytic solution is returned with a negative electrode, and metal lead deposits. This crystal grows the inside of a separator, reaches the plate of another side, and results in a short circuit.

[0010] The short circuit by the cause of the above [2] is suppressed by making the path of the micropore of a separator small and carrying out densification by mixing inorganic fine particles, such as a silica, with the separator for sealed lead acid batteries of this invention. Furthermore, by mixing the natural pulp which carried out beating, the tensile strength and penetration-proof reinforcement of a separator are raised, and the short circuit by the cause of the above [1] is suppressed. Both, since these inorganic powder and natural pulp are the high ingredients of a hydrophilic property, they do not spoil the cell engine performance of a separator.

[0011] in this invention, it is based on two causes in this way -- simplistic -- since the separator which receives and has sufficient resistance can be milled at one process, it can manufacture by low cost.

[0012] And since the separator of this invention is comparatively high-density, thinning is possible for it, and an electrode spacing can apply it effective also in 0.3-0.7mm and a narrow plate electrode.

[0013] In this invention, as a detailed glass fiber, the acid-proof glass fiber of 1 micrometer or less of diameters of average fiber is desirable, and the silica powder more than specific-surface-area of 100m 2/g is suitable as inorganic fine particles. As natural pulp, that by which beating was carried out to 250 or less mL of Canadian freshness is desirable.

[0014]

[Embodiment of the Invention] The gestalt of the operation of this invention to the following is explained to a detail. [0015] The separator for sealed lead acid batteries of this invention makes a detailed glass fiber a subject, and a consistency is a three or more 0.165 g/cm thing including 5 - 30% of the weight of inorganic fine particles, and 3 - 20% of the weight of the natural pulp which carried out beating.

[0016] In this invention, as a detailed glass fiber, the acid-proof glass fiber of 1 micrometer or less of diameters of average fiber and alkali glass fiber with especially good acid resistance are desirable, and, as for the content of this detailed glass fiber, it is desirable that it is 50 - 92 % of the weight. If the diameter of average fiber of a detailed glass fiber exceeds 1 micrometer, liquid holding power, paper-milling nature, etc. will fall. Moreover, if less than 50 % of the weight of liquid holding power is [the content] insufficient and it exceeds 92 % of the weight, the content of inorganic fine particles and natural pulp will decrease relatively, and sufficient short circuit-proof nature will not be obtained. [0017] When less than 5 % of the weight of the content of inorganic fine particles is not enough as the short circuit

prevention effectiveness and it exceeds 30 % of the weight, the rate of a detailed glass fiber or natural pulp decreases relatively, and a mechanical strength is inferior. Therefore, the content of inorganic fine particles is made into 5 - 30 % of the weight.

[0018] As these inorganic fine particles, although a silica, a titanium dioxide, diatomaceous earth, etc. can be used, it is desirable to use the silica powder more than specific-surface-area of 100m 2/g by the high hydrophilic property from the point which is low cost. If it is the silica powder more than specific-surface-area of 100m 2/g, there is much pore on the interior of a particle and the front face of a particle, and it is excellent in the solution retention improvement effectiveness of the electrolytic solution.

[0019] The content of the natural pulp which carried out beating cannot compensate enough the fall on the strength by inorganic powder mixing with less than 3 % of the weight, but the effectiveness over a short circuit is low. However, if this content exceeds 20 % of the weight, a separator will become hard too much and adhesion with a plate will fall.

Therefore, the content of natural pulp is made into 3 - 20 % of the weight.

[0020] It is desirable to use what carried out beating of the pulp of a needle-leaf tree system with the beater etc. as this natural pulp. That is, needle-leaf tree system pulp can acquire the extremely excellent reinforcement effectiveness from fiber length being long and being homogeneous. When extent of the beating is expressed with Canadian freshness (Canada standard freshness), it is desirable that 250 or less mLs are especially 150 or less mLs by 0.3-% of the weight concentration (in addition, the freshness of the natural pulp which has not carried out beating is 600 or more mLs.). If it is the natural pulp by which beating was carried out to such freshness, it has one several times the very big pore volume [usual specific surface area and pore volume] of pulp, and excels in reactivity, a hydrophilic property, water retention, etc., and acid resistance is also high, since it has the reinforcement effectiveness which was moreover excellent, the reinforcement and the degree of hardness of a separator can be remarkably increased by little addition, and solution retention and absorbency will not be spoiled.

[0021] In this invention, this natural pulp may substitute a fibrillation cellulose for that part. A fibrillation cellulose makes natural pulp detailed even to microfibril, and is effective in improvement in a mechanical strength. However, when blending a fibrillation cellulose, it is made for the loadings of the sum total with the natural pulp which made that content 5 or less % of the weight, and carried out beating to the fibrillation cellulose to become 20 or less % of the weight, since a separator will become hard too much and adhesion with a plate will fall, if the content of this fibrillation

cellulose exceeds 5 % of the weight.

[0022] The separator for sealed lead acid batteries of this invention can manufacture the above-mentioned component by following a conventional method, and mixing and milling paper preferably, or more [0.165g //cm] 3 consistency, so that it may become three or more 0.165 - 0.250 g/cm.

[0023] In this invention, the opening of a separator increases that the consistencies of a separator are less than three 0.165 g/cm, and when it considers as the separator for plate electrodes with thin thickness, sufficient short circuit-proof nature cannot be obtained. If a consistency becomes higher than 0.250 g/cm3, since solution retention etc. will fall, the consistency of a separator is preferably made into 0.165 - 0.250 g/cm3.

[0024] In this invention, even if it is the comparatively thin separator which it says is 0.4-0.8mm (thickness by the measuring method in the below-mentioned example) in thickness by considering as such a separator with a comparatively high consistency, sufficient short circuit prevention effectiveness can be acquired.

[0025] Such a separator for sealed lead acid batteries of this invention is very useful as a separator for plate electrodes.

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- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

EXAMPLE

[Example] Although an example and the example of a comparison are given to below and this invention is more concretely explained to it, this invention is not limited to the following examples, unless the summary is exceeded. In addition, the ingredient used in the following examples and examples of a comparison is as follows. [0027]

[Material of construction]

Glass fiber: 0.8 micrometers [of average fiber ****] alkali glass fiber Silica powder: Silica powder of specificsurface-area of about 200m 2/g Natural pulp which carried out beating: Needle-leaf tree system pulp Canadian freshness abbreviation 150mL What carried out beating Thermoplastic organic fiber: It is about 5m in 20 micrometers of average fiber ****, and fiber length. Polyester fiber The separator for batteries was manufactured by the ingredient combination shown in one to examples 1 and 2 and example of comparison 4 table 1, and measurement results, such as many of the properties, were shown in Table 1. In addition, each measuring method etc. is as follows. [0028] ** Thickness (mm) and a consistency (g/cm3)

It asked for thickness T (SBA4501) which measured the sample in the condition of having pressed by the pressure of 0.2 kgf/cm2 in the thickness direction, and the consistency was computed by W/(TxS) from the mass W measured with this thickness T and an electronic balance, and the area S of a sample.

** Tensile strength (gf/10mm2)

It is based on SBA4501.

** Measure the maximum load at the time of forcing perpendicularly the needle which has a spherical tip at the rate of 120 mm/min to the fixed sample, and penetrating by 1mm of penetration sizes on the strength. Since this measured value was influenced by the form letter rack with a minute needle tip, relative evaluation was made on the result of the example 1 of a comparison as 100 in the ratio with the measured value in a standard sample (thing of the example 1 of [0029] ** Absorbency (mm/min)

A sample is made perpendicular, the lower part is immersed in the dilute sulfuric acid of specific gravity 1.30, and it

asks by measuring the liquid level which goes up in 1 minute from the time of immersion.

[0030] ** Between the monotonous lead electrode plates (an electrode area of about 7mm 2) of two electrochemical short circuit duration, it arranges on both sides of a separator with a thickness of 0.5mm, and is immersed into the saturated solution of a lead sulfate. Furthermore, where the pressure force of 0.3 kgf/m2 is applied, regularity electricalpotential-difference 10V are impressed to this. If the metal lead which grew from the negative electrode reaches a positive electrode, since inter-electrode resistance will decrease rapidly, this time amount is measured and it is the thickness of a separator, and it is ****. This measured value made relative evaluation on the result of the example 1 of a comparison as 100 in the ratio with the measured value in a standard sample (thing of the example 1 of a

[0031] Penetration reinforcement is the index of a mechanical short circuit among the above-mentioned characterization, and a mechanical short circuit cannot occur easily, so that penetration reinforcement is high. Moreover, electrochemical short circuit duration is excellent in the short circuit prevention effectiveness, so that it is

[0032]

[Table 1]

	. •	美	施例		比較例		
-	·	1	2	1	2	3	4
配合(新	ガラス繊維	80	75	100	80	75	90
	シリカ粉末	10	20			20	
重量%	叩解パルブ	10	5				10
Ľ	熱可塑性 有機械維				20	5	1
	厚さ (mm)	0.5	0.5	0.5	0.5	0.5	0.5
	密度 (g/am³)	0.18	0.20	0.14	0.15	0.20	0.15
特性	引張強度 (gf/10mm²)	480	360	440	660	300	720
等	貫通強度 ※	190	120	100	270	70	200
	吸液性 (mm/min)	50	50	50	40	45	50
	電気化学的 短絡時間 ※	4500	6000	100	250	1600	300

※ : 比較例1の結果を100とする相対値。

[0033] The following thing is clearer than Table 1.

[0034] That is, in the example 1 of a comparison of only a glass fiber, penetration reinforcement is low and its short circuit duration is also short. In the example 2 of a comparison of only a glass fiber and organic fiber, although penetration reinforcement is high, short circuit duration is comparatively short, and absorbency is also inferior in it. In duration is long, penetration reinforcement is very low. In the example 4 of a comparison of only a glass fiber and beating pulp, penetration reinforcement is high, and although absorbency is also good, short circuit duration is comparatively short.

[0035] on the other hand, in the examples 1 and 2 which blended a glass fiber, silica powder, and beating pulp at a predetermined rate, without spoiling absorbency, high penetration reinforcement and long short circuit duration are filled to coincidence, and it is based on the two above-mentioned causes — simplistic — it receives and is very effective.

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(54) 【発明の名称】 密閉型鉛蓄電池用セパレータ

(57)【要約】

【課題】 微細ガラス繊維を主体とし、無機粉体及び天然パルプを混合することにより、電池の正極板と負極板とを間の電気的短絡に対する耐性を向上させた密閉型鉛蓄電池用セパレータであって、密度を高めることにより、より一層の薄肉化を可能とし、平板電極へも有効に適用可能とした密閉型鉛蓄電池用セパレータを提供する。

【解決手段】 微細ガラス繊維を主体として構成され、無機粉体と、叩解した天然パルプとを含む密閉型鉛蓄電池用セパレータ。無機粉体の含有量が5~30重量%、天然パルプの含有量が3~20重量%であり、密度が0.165g/cm³以上である密閉型鉛蓄電池用セパレータ。

【特許請求の範囲】

【請求項1】 微細ガラス繊維を主体として構成され、 無機粉体と、叩解した天然パルプとを含む密閉型鉛蓄電 池用セパレータにおいて、

該無機粉体の含有量が5~30重量%で、該天然パルプ の含有量が3~20重量%であり、密度が0.165g /cm³以上であることを特徴とする密閉型鉛蓄電池用 セパレータ。

【請求項2】 請求項1において、該微細ガラス繊維が 特徴とする密閉型鉛蓄電池用セパレータ。

【請求項3】 請求項1又は2において、該無機粉体が 比表面積100m2/g以上のシリカ粉末であることを 特徴とする密閉型鉛蓄電池用セパレータ。

【請求項4】 請求項1ないし3のいずれか1項におい て、該天然パルプが、カナディアン沪水度250mL以 下に叩解されたものであることを特徴とする密閉型鉛蓄 電池用セパレータ。

【発明の詳細な説明】

[0001]

【発明の属する技術分野】本発明は密閉型鉛蓄電池用セ パレータに係り、特に、微細ガラス繊維を主体とし、無 機粉体及び天然パルプを混合することにより、電池の正 極板と負極板との間の電気的短絡に対する耐性を向上さ せた密閉型鉛蓄電池用セパレータに関する

[0002]

【従来の技術】密閉型鉛蓄電池用セパレータの形態とし ては、主にガラス繊維から構成されるシート状セパレー 夕が一般的である。しかし、従来のセパレータでは、極 板の突起の局部的圧迫による貫通や断裂、或いは充電時 30 のセパレータ内部における金属鉛の結晶成長等により、 正極板と負極板とが電気的に短絡し、その結果、蓄電池 の充放電ができなくなるという現象が見られた。これ は、従来のセパレータは、機械的強度が比較的低いた め、電極の突起で貫通、断裂し易いこと、また、密度が 比較的低く、孔径が比較的大きいため、極板からの金属 鉛の成長も起き易いことによるものであり、このような 現象は、セパレータの厚みが薄くなると、機械的強度が より低下する上に、正極と負極との間の距離が短くなる ため、より一層顕著なものとなる。

【0003】この電気的短絡の原因のうち、金属鉛の結 晶成長は、セパレータを高密度化して、空隙を減少さ せ、セパレータ内での結晶の成長を阻害することによっ て改善できるものと考えられる。そのための手段として は、例えばガラス繊維間にシリカ等の無機粉体を保持す ることが考えられる。しかしながら、無機粉体を混合す ると、その分ガラス繊維量が減ることでガラス繊維同士 の絡み合いが減少し、その結果、機械的強度が著しく低 下することにより電極の突起の圧迫に起因する電気的短 絡が起き易くなる。

【0004】一方、セパレータの貫通、断裂は、セパレ ータの機械的強度を向上させることによって改善され る。そのための手段としては、合成繊維を混合する方法 が公知である(例えば、特開昭54-22531号公 報、特開昭56-99968号公報、特公昭58-66 3号公報)。しかし、合成繊維はガラス繊維に比べて親 水性が低いため、合成繊維を混抄したセパレータは硫酸 液の吸液性、保液性が劣るという欠点を有する。

【0005】また、叩解セルロースを混合する方法も公 平均繊維径1μm以下の耐酸性ガラス繊維であることを 10 知であり(特開昭64-52375号公報)、この場合 には、吸液性、保液性を損なうことなく機械的強度を向 上させることができる。しかし、叩解セルロースの混合 による密度変化はわずかであるため、金属鉛の結晶成長 による短絡を抑えることはできない。

[0006]

【発明が解決しようとする課題】本発明は、上記従来の 問題点を解決し、微細ガラス繊維を主体とし、無機粉体 及び天然パルプを混合することにより、電池の正極板と 負極板との間の電気的短絡に対する耐性を向上させた密 20 閉型鉛蓄電池用セパレータであって、密度を高めること により、より一層の薄肉化を可能とし、平板電極にも有 効に適用可能とした密閉型鉛蓄電池用セパレータを提供 することを目的とする。

[0007]

【課題を解決するための手段】本発明の密閉型鉛蓄電池 用セパレータは、微細ガラス繊維を主体として構成さ れ、無機粉体と、叩解した天然パルプとを含む密閉型鉛 蓄電池用セパレータにおいて、該無機粉体の含有量が5 ~30重量%で、該天然パルプの含有量が3~20重量 %であり、密度が0.165g/cm³以上であること を特徴とする。

【0008】密閉型鉛蓄電池における正極と負極との間 の電気的短絡は、多くの場合、次の2つの原因によって

【0009】[1] 機械的短絡:極板に突起物(格子 の凹凸、活物質の粒状塊等)があった場合、局所的な圧 **迫力や剪断力が生じる。この力に比してセパレータの強** 度が弱ければ、貫通又は断裂が起き、突起が他方の極板 と接触して短絡に至る。

[2] 電気化学的短絡:放電末期、電解液中の硫酸イ オンが消費され、電解液が純水に近くなると、鉛イオン の溶解度が大きくなり、正極と負極に生成した硫酸鉛が 一部溶解する。この後に充電すると、電解液中の鉛イオ ンが負極で還元されて金属鉛が析出する。この結晶がセ パレータ中を成長し、他方の極板に到達し、短絡に至 る。

【0010】本発明の密閉型鉛蓄電池用セパレータで、 シリカ等の無機粉体を混合することで、セパレータの微 細孔の径を小さくして、高密度化することにより、上記 50 [2]の原因による短絡を抑える。更に、叩解した天然 パルプを混合することにより、セパレータの引張強度及び耐貫通強度を向上させ、上記[1]の原因による短絡を抑える。これら無機粉末及び天然パルプは、共に、親水性の高い材料であるため、セパレータの電池性能を損うことはない。

【0011】本発明では、このように2つの原因による 短絡に対して十分な耐性を有するセパレータを1つの工 程で抄造できるため、低コストで製造可能である。

【0012】しかも、本発明のセパレータは、比較的高密度であるため薄肉化が可能で、電極間隔が0.3~0.7mmと狭小な平板電極にも有効に適用することができる。

【0013】本発明において、微細ガラス繊維としては、平均繊維径1μm以下の耐酸性ガラス繊維が好ましく、無機粉体としては比表面積100m²/g以上のシリカ粉末が好適である。天然パルプとしては、カナディアン沪水度250mL以下に叩解されたものが好ましい。

[0014]

【発明の実施の形態】以下に本発明の実施の形態を詳細 20 に説明する。

【0015】本発明の密閉型鉛蓄電池用セパレータは、 微細ガラス繊維を主体とし、5~30重量%の無機粉体 と3~20重量%の叩解した天然パルプとを含み、密度 が0.165g/cm³以上のものである。

【0016】本発明において、微細ガラス繊維としては、平均繊維径1μm以下の耐酸性ガラス繊維、特に、耐酸性が良好な含アルカリガラス繊維が好ましく、この微細ガラス繊維の含有量は、50~92重量%であることが好ましい。微細ガラス繊維の平均繊維径が1μmを 30超えると、液保持力や抄造性等が低下する。また、その含有率が50重量%未満では、液保持力が不十分であり、92重量%を超えると相対的に無機粉体及び天然パルプの含有量が低減して十分な耐短絡性が得られない。【0017】無機粉体の含有量が5重量%未満では、短絡防止効果が十分でなく、30重量%を超えると相対的に微細ガラス繊維や天然パルプの割合が低減して機械的強度が劣るものとなる。従って、無機粉体の含有量は5~30重量%とする。

【0018】この無機粉体としては、シリカ、二酸化チ 40 タン、ケイ藻土等を用いることができるが、高親水性で低コストである点から、比表面積100m²/g以上のシリカ粉末を用いることが好ましい。比表面積100m²/g以上のシリカ粉末であれば、粒子内部及び粒子表面の細孔が多く、電解液の保液性の向上効果に優れる。【0019】叩解した天然パルプの含有量が3重量%未満では、無機粉体混合による強度低下を十分補えず、短絡に対する効果が低い。しかし、この含有量が20重量%を超えると、セパレータが硬くなり過ぎ、極板との密着性が低下する。従って、天然パルプの含有量は3~2 50

0重量%とする。

【0020】この天然パルプとしては、針葉樹系のパルプをビーター等により叩解したものを用いるのが好ましい。即ち、針葉樹系パルプは繊維長が長く、均質であることから、極めて優れた補強効果を得ることができる。その叩解の程度は、カナディアン沪水度(カナダ標準沪水度)で表わした場合、0.3重量%濃度で250mL以下、特に150mL以下であることが好ましい(なお、叩解していない天然パルプの沪水度は600mL以10上である。)。このような沪水度に叩解された天然パルプであれば、通常のパルプの数倍の非常に大きな比表面積及び細孔容積を有し、反応性、親水性、保水性等に優れ、耐酸性も高く、しかも優れた補強効果を有するため、少量添加でセパレータの強度及び硬度を著しく増大させることができ、保液性、吸液性を損なうことはない。

4

【0021】本発明において、この天然パルプは、その一部をフィブリル化セルロースで代替しても良い。フィブリル化セルロースは天然パルプをミクロフィブリルにまで微細化したものであって、機械的強度の向上に有効である。ただし、このフィブリル化セルロースの含有量が5重量%を超えるとセパレータが硬くなり過ぎ、極板との密着性が低下するため、フィブリル化セルロースを配合する場合、その含有量は5重量%以下とし、フィブリル化セルロースと叫解した天然パルプとの合計の配合量が20重量%以下となるようにする。

【0022】本発明の密閉型鉛蓄電池用セパレータは、 上記の成分を密度0.165g/cm³以上、好ましく は、0.165~0.250g/cm³以上となるよう に常法に従って混合、抄造することにより製造すること ができる。

【0023】本発明において、セパレータの密度が0.165g/сm³未満であると、セパレータの空隙が多くなり、厚さの薄い平板電極用セパレータとした場合に十分な耐短絡性を得ることができない。密度が0.250g/сm³より高くなると、保液性等が低下するため、セパレータの密度は好ましくは0.165~0.250g/сm³とする。

【0025】このような本発明の密閉型鉛蓄電池用セパレータは、平板電極用セパレータとして極めて有用である。

[0026]

【実施例】以下に実施例及び比較例を挙げて本発明をより具体的に説明するが、本発明はその要旨を超えない限り以下の実施例に限定されるものではない。なお、以下

の実施例及び比較例で用いた材料は次の通りである。 * *【0027】

[使用材料]

ガラス繊維

: 平均繊維径約0.8 μmの含アルカリガラス繊維

シリカ粉末

: 比表面積約200m2/gのシリカ粉末

叩解した天然パルプ:針葉樹系パルプをカナディアン沪水度約150mL

に叩解したもの

熱可塑性有機繊維 :平均繊維径約20μm、繊維長さ約5mの

ポリエステル繊維

実施例1,2、比較例1~4

その諸特性等の測定結果を表1に示した。なお、各測定 法等は下記の通りである。

[0028] 0 厚さ(mm)及び密度(g/c m^3)

試料を厚み方向に O. 2kgf/cm²の圧力で押圧し た状態で測定した厚みT(SBA4501)を求め、こ の厚みTと電子天秤にて測定した質量Wと、試料の面積 Sから、密度をW/(T×S)で算出した。

引張強度(gf/10mm²) SBA4501による。

(3) 貫通強度

[0029] 4

太さ1 mmで球状の先端を有するニードルを、固定した 試料に対して垂直方向に、120mm/minの速度に て押し付け、貫通する際の最大荷重を測定する。本測定 値はニードル先端の微小な形状差に影響されるので、標 準試料(比較例1のもの)での測定値との比にて比較例 1の結果を100として相対評価した。

吸液性(mm/min)

※試料を垂直にしてその下部を比重1.30の希硫酸に浸 表 1 に示す材料配合にて蓄電池用セパレータを製造し、 10 潰し、浸漬時より 1 分間に上昇する液位を測定すること により求める。

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[0030] 電気化学的短絡時間 2つの平板鉛電極板(電極面積約7 m m²)の間に、厚 み0.5mmのセパレータを挟んで配置し、硫酸鉛の飽 和溶液中に浸漬する。更に、0.3kgf/m2の圧迫 力を加えた状態で、これに一定電圧10Vを印加する。 負極より成長した金属鉛が正極に到達すると、電極間の 抵抗値が急激に減少するので、この時間を測定し、セパ

レータの厚みで除す。本測定値は、標準試料(比較例1 20 のもの)での測定値との比にて、比較例1の結果を10 0として相対評価した。

【0031】上記特性評価のうち、貫通強度は、機械的 短絡の指標であって、貫通強度が高いほど機械的短絡は 起きにくい。また、電気化学的短絡時間は長いほど短絡 防止効果に優れる。

[0032]

【表1】

		実	施例		比較例		
├—		· 1	2	1	2	3	1 4
配合(音	ガラス繊維	80	75	100	80	75	90
	シリカ粉末	10	20			20	
重量%	叩解パルブ	10	5				10
Ü	熱可塑性 有機機維				20	5	
	厚さ (mm)	0.5	0.5	0.5	0.5	0.5	0.5
	密度 (g/am³)	0.18	0.20	0.14	0.15	0.20	0.15
特性等	引張強度 _(gf/10mm²)	480	360	440	660	300	720
	貫通強度 ※	190	120	100	270	70	200
	吸液性 (mm/min)	50	50	50	40	45	50
	電気化学的 短絡時間 ※	4500	6000	100	250	1600	300

※ : 比較例1の結果を100とする相対値。

【0033】表1より次のことが明らかである。 【0034】即ち、ガラス繊維のみの比較例1では、貫 通強度は低く、短絡時間も短い。ガラス繊維と有機繊維 のみの比較例2では、貫通強度は高いが、短絡時間は比

★末と有機繊維を配合した比較例3では、短絡時間は長い が、貫通強度が極めて低い。ガラス繊維と叩解パルプの みの比較例4では、貫通強度は高く、吸液性も良好だ が、短絡時間が比較的短い。

較的短く、また、吸液性も劣る。ガラス繊維とシリカ粉★50 【0035】これに対して、ガラス繊維とシリカ粉末と

叩解パルプとを所定割合で配合した実施例1,2では、 吸液性を損なうことなく、高い貫通強度と長い短絡時間 を同時に満たし、前述の2つの原因による短絡に対して 極めて有効である。

[0036]

【発明の効果】以上詳述した通り、本発明の密閉型鉛蓄 電池用セパレータによれば、次のような効果が奏され、 密閉型鉛蓄電池の正極板と負極板との電気的短絡が起き 難く、吸液性能等のセパレータ特性にも優れる上に、安 価な密閉型鉛蓄電池用セパレータが提供される。本発明 10 (3) 親水性の高い材料のみで構成されているため、 の密閉型鉛蓄電池用セパレータは、特に、高特性平板電 極板用セパレータとしてその薄肉化に極めて有効であ る。

【0037】(1) セパレータのガラス繊維間に無機 粉末が保持され、高密度である。セパレータの細孔中の 無機粉末は金属鉛の結晶成長を妨げる働きをする。ま た、叩解した天然パルプの微細繊維も同様の働きをす る。このため、金属鉛の結晶成長による電気的短絡が起

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- (2) 叩解した天然パルプがセパレータの機械的強 度、特に貫通強度を向上させる。このため、電極板の突 起での局所的圧迫力による貫通、断裂が起き難い。
- 親水性、保液性が高く、電池性能が良好である。
- (4) 単一の混合、抄造工程で容易に製造することが でき、低コストである。